

Table 4.1 Food characteristics influenced by oxygen scavengers

Characteristic	Targets
Microbiological status	Moulds, aerobic bacteria
Infection	Insects, larvae, eggs
Chemical degradation	Rancidity, pigment/nutrient loss, browning
Physiological changes	Respiration

of the problems of distribution of oxygen-sensitive foods as described by Brody (1989). However, the opportunity to improve on the benefits gained by application of those technologies, as well as the chance to treat the problems of distribution of foods individually, has led to the current interest in oxygen-scavenging plastics.

The properties of foods that can be influenced by the presence of oxygen scavengers are shown in Table 4.1. The growth of moulds is particularly important in dairy products such as cheese and in bakery products. Oxygen levels of 0.1% or lower are required to prevent the growth of many moulds. Bacterial growth and the growth of yeasts can be a problem in high water-activity foods including meats and prepared dishes, as well as in juices. Oxygen scavengers can prevent oxidative damage to flavour and colour in a wide range of foods. Likewise, they can maintain atmospheres with oxygen concentrations too low for insect survival in agricultural and horticultural products. The list in Table 4.2 is indicative of the range of foods which could benefit from oxygen scavenging, their type of packaging and the forms in which the scavenger might be applied. The package converter can decide the nature and quantity of active components used in plastics packaging. This allows the opportunity for tailoring the packaging to the requirements of the product.

Table 4.2 Potential applications of oxygen scavenging plastics

Product	Packaging	Component
Aspic liquids	Cartonboard, bag-in-box	film, coating, adhesive, ink
Bakery products	Flexibles	film, etc.
Beverages	Flexibles, bag-in-box	film, etc.
Beer	Crown seal liners	Resin, organosol
Cheese	Flexibles	film, etc.
Coffee, tea	Closures, flexibles	film, etc., resin
Cereals	Flexibles	film, etc.
Dried Fruit	Flexibles	film, etc.
Dried Foods/Naufs	Flexibles, closures	film, etc., resin
Fried snacks	Flexibles	film, etc.
Fruit/Vegetables	Flexibles	film, etc.
Milk powder	Flexibles	film, etc.
Meat - fresh	Flexibles	film, etc.
- processed	Flexibles	film, etc.
Pasteurised liquids	Closures, bottles	resin
Retorted foods	Can lacquers, trays, lidding	resin, film, etc.

4 Active packaging in polymer films

M.L. ROONEY

4.1 Introduction

Polymers constitute either all or part of most primary packages for foods and beverages and a great deal of research has been devoted to the introduction of active packaging processes into plastics. Plastics are thermoplastic polymers containing additional components such as antioxidants and processing aids. Most forms of active packaging involve an intimate interaction between the food and its package so it is the layer closest to the food that is often chosen to be active. Thus polymer films potentially constitute the position of choice for incorporation of ingredients that are active chemically or physically. These polymer films might be used as closure wads, lacquers or enamels in cans and as the waterproof layer in liquid cartonboard, or as packages in their own right.

The commercial development of active packaging plastics has not occurred evenly across the range of possible applications. Physical processes such as microwave heating by use of susceptor films and the generation of an equilibrium modified atmosphere (EMA) by modification of plastics films have been available for several years. Research continues to be popular in both these areas. Chemical processes such as oxygen scavenging have been adopted more rapidly in sachet form rather than in plastics. Oxygen scavenging sachets were introduced to the Japanese market in 1978 (Abe and Kondoh, 1989) whereas the first oxygen-scavenging beer bottle closures were used in 1989 (see Chapter 8). The development of plastics active packaging systems has been more closely tied to the requirements of particular food types or food processes than has sachet development.

This chapter surveys the range of polymer-based active packaging processes that have been reported, their chemical or physical basis and their application to foods and beverages. Attention is given to opportunities for, and obstacles to, either commercialisation or extension of the current range of application. Some processes which have become economically important are treated individually in other chapters.

4.2 Oxygen scavenging

The removal of oxygen from package headspaces and from solution in foods and beverages has long been a target of the food technologist. Introduction of vacuum packaging and inert-gas flushing has provided solutions for some

Wagner (1990) lists a wide range of oxygen-sensitive prepared foods which are of increasing importance in consumer societies. Some are suitably packaged using existing processes. However, quality can often be retained longer if residual oxygen is removed. This would allow use of different packaging materials and distribution systems. Some foods, and particularly beverages, cannot be stabilised adequately with existing packaging technologies in order to allow use of the full range of desired distribution systems. This is particularly important when reduced levels of additives have been chosen for regulatory or marketing reasons.

Koros (1990) has set out the maximum quantity of oxygen which a generalised range of foods can take up and still have a shelf-life of one year. These quantities are generally in the 1–200 mg/kg range. Abe and Konnoh (1989) have shown the need for oxygen removal by in-pack systems when the economic limit of around 0.5% is reached in the general case. This figure can vary in practice as residue levels of around 2% are often encountered when form-fill-seal (ffs) gas flushing is used commercially. Alternatively, less than 0.1% oxygen can be found in vacuum packs of beef primals where muscle respiration and bacterial action scavenge oxygen.

The most appropriate method of removal of oxygen from a food package depends on the nature of the food, its prior processing and the packaging machinery and the way it is distributed. The factors which may need to be considered, and estimates of efficiency when sachets are used, are summarised in Table 4.3 which is based on a similar table devised by Hirata (1992), who compared sachet technologies with vacuum and gas-flush packaging systems. The expected benefits of use of oxygen-scavenging plastics are to minimise the materials cost by matching the quantity of scavenger to the need, and to keep the filling speed high.

4.2.1 Forms of oxygen-scavenging packaging

In-pack oxygen scavenging involves use of a variety of forms of scavenger. Sachets merely inserted into the food package constitute most of the present systems in commerce. Alternatively, the scavenger can be hot-melt bonded to the inner wall of the package. This is done using the Mitsubishi Ageless scavenger sachet attached to the lid of the steamed rice packages

Table 4.3 Comparison of headspace oxygen removal systems

System	Residual O_2 , kPa	Capital investment	Film cost	Filling speed
a Vacuum	< 1.5	High	High	Low
b N ₂ Flush	1–2	Medium	High	Medium
c a + b	< 1.0	High	High	Low
d Scavenger	< 0.1	Low	Medium	High
e b + d	< 0.1	Medium	Medium	Medium

manufactured in Japan by Ajinomoto under the Take Out brand name. The self-adhesive label concept of US company Multiform Desiccants is used in the Marks & Spencer retail chain's preserved meat packs in the UK.

Beyond the concept of adhesion of sachets to the package lies a wide range of possibilities and it is to this area that much of the recent research and development has been directed. Alternatives include package inserts in the form of cards or sheets, or layers coated onto the inner wall of the package. An example is the beverage crown seal liner currently used in the beer industry. This liner was developed by Advanced Oxygen Technologies Inc. and Zapala Industries Inc. under the name SmartCap and independently by W.R. Grace and Company and under the name Daraform. Both companies manufacture in the USA. Alternatively an iron-based system has been developed under the name Oxyguard by Toyo Seikan Kaisha Ltd in Japan. The industrial development and history of oxygen-scavenging closures is discussed in detail in Chapter 8.

Oxygen-scavenging films or other plastics packaging materials are alternatives to sachets. Low molecular weight ingredients may be dissolved or dispersed in a packaging plastic or the plastic may be made from a polymeric scavenger. The scavenger may be incorporated into a solid which is dispersed in the plastic or may be introduced into various layers of the package such as in the form of adhesive, printing ink, lacquer or enamel, such as found in cans.

Sachets can be a highly efficient form of oxygen scavenger but their nature does not favour contact with liquid foods or where cling of the package to the film may isolate the sachet from areas of oxygen entrapment or ingress. In such situations it would be preferable to have the scavenger in the packaging material. This allows all exposed surfaces of the food to be deoxygenated or protected from oxygen ingress by permeation.

4.2.2 Plastics packaging as media for oxygen scavenging

Oxygen-scavenging packaging has to date been applied only in packs which have inherently a substantial barrier to oxygen ingress by permeation or leakage. Abe and Kondoh (1989) recommend that Ageless sachets should be used in packages with an oxygen transmission rate less than 20 ml/m²/atm/day. Such requirements therefore rule out the common heat-seal polymers and thin layers of the more mediocre barriers like polyester (PET) and nylon 6. However, there can be situations such as in transportation of beef primal cuts in which a shorter period of absolute barrier to oxygen is desirable and these plastics might be used as the barrier. The patent of Speer and Roberts (1993) describes a system involving oxidation of poly(1,2-butadiene) and appears to be directed at that market.

The commonly found oxygen barriers may be in the form of a single-layer package, as in the case of the PET or PVC bottle, or jar or cup, but are more

Table 4.4 Permeability coefficients $P \times 10^4$ ($\text{cm}^3 \text{ mm cm}^{-2} \text{ sec}^{-1} \text{ cm}^{-1} \text{ Hg}$) @ 30°C

Film material	N_2	O_2	CO_2
Polyvinylidene chloride	0.0094	0.033	0.29
Polyester (Mylar A)	0.05	0.22	1.53
Polyamide (Nylone 6)	0.10	0.38	1.6
Polyethylene (d = 0.960)	2.7	10.6	35
Polyethylene (d = 0.922)	19	53	152
Polystyrene	2.9	11.0	88
Polyvinylchloride	0.40	1.2	10

(Reproduced from Price, 1962, with permission.)

likely be part of a multilayer package. Table 4.4 shows the oxygen permeability of a range of polymers. A more extensive tabulation of film permeability values can be found in the review by Bixler (1971).

Oxygen-scavenging compounds can be dispersed or blended in high-permeability films such as plasticised PVC and polyethylene. Where the oxygen scavenger is molecularly dispersed in the polymer it is available to oxygen in its entirety, unlike the case where solid particles are used. The particular advantage of such polymers is that they allow rapid diffusion of oxygen and water (at elevated temperatures) from the headspace or food in to the reactive ingredients. Such a characteristic of the polymer helps offset the disadvantage of plastics-film-based compositions in comparison with sachets where the scavenging powder has a large reactive surface area exposed. Polyethylene and polyvinyl chloride (plasticised) are nominated as the reaction medium in crown closure liners for beverage bottles such as for beer, as described in detail in Chapter 8.

The use of plastics as media in which to disperse or dissolve oxygen scavengers places a severe limitation on the number of reactions which can be involved in the scavenging process. Whereas molecules of the size of oxygen or water can diffuse at an adequate rate, larger molecules behave as if they were immobilised. The fact that a molecule can migrate fast enough to fail food-contact regulatory tests does not indicate that it can be used in an oxygen-scavenging system. Thus the use of iron oxidation in polymers has been a challenge for some years requiring all reagents to be intimately mixed. A further challenge is to establish whether the breakdown of iron particles on oxidation occurs as freely in a polymer matrix as it does in powder form in sachets. Labuza and Breene (1989) note that virtually all of the iron in commercial sachets is available for oxygen removal.

The high gas and vapour permeability of the common heat-seal polymers allows them to be used as reaction media for oxygen scavenging in laminates. Indeed this has been proposed in a large number of patents such as those of Hofeldt and White (1989) and Farrell and Tsai (1985). The presence of the oxygen scavenger in the heat-seal layer allows maximum advantage to be taken of the full thickness of the physical barrier to oxygen permeation of the barrier layer. However, if the scavenger is incorporated

into the barrier layer as in the Ox-bar bottle of CMB Technologies plc (Rolland, 1990) that portion closer to the outside becomes exposed to relatively large amounts of oxygen.

The permeability of the polymer medium in which the scavenging reaction occurs need not be the limiting variable determining scavenging rate. Depending upon the chemistry involved, the oxidation reaction can be inherently slow, as with crystalline sulfites at room temperature or the reaction can require the presence of an additional species as with the rusting of iron. The permeability of the heat-seal layer to both oxygen and water vapour can be limiting as in the mixed sulfite/acetate layer in retort pouches patented by Farrell and Tsai (1985). In this case the water is needed in substantially larger quantity than the oxygen in order to dissolve the deliquescent potassium acetate in which solution the potassium sulfite dissolves and reacts with oxygen.

An approach to overcoming any limitation on scavenging rate by the heat-seal layer's permeability has been to use microporous polymers such as non-woven polyolefins. Several recent patent applications describe claims of enhanced availability to the package atmosphere of granular reagents, as in that of Mitsubishi Gas Chemical Industry Co. Various sulfites can be held in a fibrous layer sandwiched between, for example, one layer of foil, and a second of a plastic or paper with an oxygen permeability greater than 7000 $\text{ml/m}^2/\text{day atm}$. A second patent describes a package consisting of three layers. The outer layer is a plastics film, the middle is a perforated or non-woven layer containing an oxygen scavenger and the inner layer of the package is a microporous film which resists the flow of liquids through its pores. This is claimed to be useful for packaging liquid foods (Ohtsuka *et al.*, 1984). Such films cannot be used where transparency is required but may have application in many forms of packaging.

Traditionally, poly(vinylidene chloride) copolymers have provided a water-insensitive oxygen barrier when used as a layer in laminates, coated films or coextrusions. The introduction of ethylene-vinyl alcohol copolymers (EVOH) and poly(vinyl alcohol) means that, together with traditional nylons, most oxygen barriers are now water sensitive. The permeability to oxygen of EVOH copolymers increases approximately 10-fold when exposed to a relative humidity change from about 40–100%. Such a change may render a material which is suitable for packaging an oxygen-sensitive food at low relative humidity into one which is most unsuitable at high relative humidity.

The plasticising effect of water on the barrier properties of EVOH (or other hydrophilic barriers) is time dependent, especially if the hydrophilic layer is protected by a water-barrier layer such as polypropylene as in the case of retortable lunch-cups. When such retortable packs containing a wet food such as an entrée are subjected to steam retorting, water is absorbed by the EVOH in such large quantities that the barrier layer becomes quite

permeable to oxygen. The rate of water release through the outer polypropylene layer becomes very slow on cooling, so the oxygen permeability can remain elevated for many weeks (Tsai and Wachtel, 1990). Although addition of desiccants to the polypropylene (Tsai and Wachtel, 1990) and mica platelets to the EVOH (Bisson, 1990) is used to reduce this impact there is an opportunity here to include an oxygen-scavenger layer in the coextrusion to absorb the oxygen, particularly during the period of enhanced permeability. In fact there has been a recent news report of the introduction of an oxygen scavenger into such packages by Toyo Seikan Kaisha Ltd. This active packaging has the potential to contribute to solving the permeability problem in two ways, providing: desiccants which absorb water in polypropylene; and oxygen scavengers which remove oxygen when it does pass through the hydrated barrier layer.

Whereas elevated temperatures and high humidity have been used to advantage in the research of Farrell and Tsai (1985), the effect of temperature on the performance of oxygen scavengers in polymer-based films has been reported in only rare cases. W.R. Grace (1994) have investigated the effect of low temperatures on their (optionally photosensitised) metal-catalysed oxidation of syndiotactic poly(1, 2-butadiene). They have found that this polymer, and certain other low crystallinity polymers with glass transition temperatures below -15°C , scavenge at least $10\text{ mL/m}^2/\text{day O}_2$ at 10°C or lower. The photoinitiated system described by Rooney (1994) has been shown to function at 0°C .

4.2.3 Brief history of oxygen-scavenging films

The initial oxygen-scavenging packaging film was a multilayer described by Kuhn *et al.* (1970) and by Warmbier and Wolf (1976). These systems were based on the earlier work of King (1955) and Abbott *et al.* (1961) who applied palladium metal to the inside surface of can lids. The cans were flushed with mixtures of hydrogen (8%) in nitrogen to give a mixture in which the residual oxygen could react with hydrogen to form water on the palladium surface.

The reaction of hydrogen with residual oxygen on palladium has been taken further by Hayashi *et al.* (1986) who vacuum-metallised polyester film at 2.5×10^{-4} moles of Pd/m^2 and laminated this to high density polyethylene. When a bag made from this laminate was filled with 500 ml of a mixture of hydrogen-nitrogen 8.92% by volume, this layer was found to be effective in catalysing the conversion of oxygen to water, reducing the oxygen content from 3.4 to 0.4% in 1 day. Due to the expense of this process it would be suitable for packaging high-valued items such as probes for an oxygen analyser, although production of a thinner metal layer may change future economics.

The earliest investigation involving reaction of oxygen in homogeneous

polymer films was described by Rooney and Holland (1979). Rooney, Holland and Shorter (1981) and by Rooney (1981, 1982). This technique takes advantage of the ease of excitation of oxygen from its ground state to its first singlet excited state and has shown that use of polymers as scavengers or reaction media need not inhibit rapid oxygen removal.

Very little investigation of the chemistry of oxygen-scavenging films has been published in peer-reviewed journals. However, numerous patents and some conference proceedings give sufficient detail to allow a comparison of the systems reported. The most evident trend in oxygen-scavenging system development during the past 20 years has been the increasing importance of patent applications for compositions and designs based on plastics. Very few of these have involved actual polymer oxidation but rather have required the reactive ingredients to be dispersed within the polymer matrix or to be sandwiched between film layers. An examination of patent applications worldwide gives the results shown in Figure 4.1 which shows the numbers of initial applications for new compositions or designs without consideration of whether additional applications for the same idea have been lodged in other countries. The histogram shows that whereas initially only sachet technologies were considered, there was a slow growth in the number of plastics-based systems devised until the numbers were equal for both types of system in 1993-94.

The increasing number of plastics-based systems results from a substantial overall increase in the interest in oxygen-scavenging systems, not from a decrease in the numbers of sachet technology applications. This has resulted from a more lateral approach to potential reactions coupled with approaches

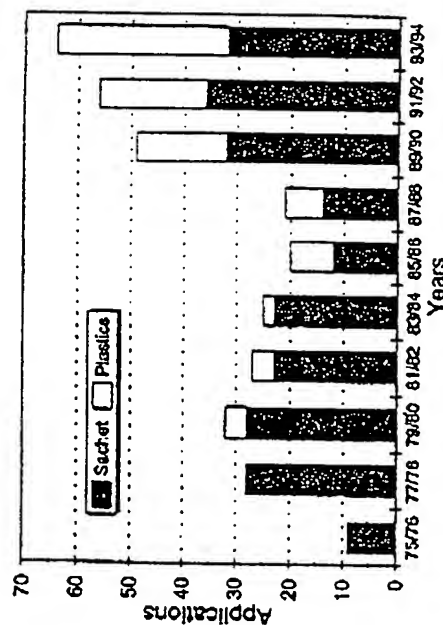


Figure 4.1 Patent applications for oxygen scavengers involving sachets and plastics.

to overcoming previous deficiencies. This is particularly evident in patent applications for systems involving oxidation of carbon-carbon double bonds in small molecules like squalene and fatty acids or in polymers like rubbers. In each case the transition-metal catalysed oxidation results in development of odorous compounds such as low molecular weight aldehydes which are adsorbed by zeolites, carbon or other adsorbents. In one example linseed oil, iron oleate, calcium carbonate and active clay are mixed with activated carbon to give a solid oxygen scavenger (Toppan, 1992). The advantage of this system is that water is not needed as a reagent. Some compositions, such as that of W.R. Grace and Co. for oxidation of squalene with a transition metal catalyst (Ehner *et al.*, 1992), appear not to include an adsorbent for odorous products. Some patents involve claims of conventional antioxidants as oxygen scavengers. The use of bifunctional antioxidants at up to 2% in rigid poly(vinyl chloride) was claimed to reduce the permeability of that polymer 20-fold although the period of effectiveness was not reported (Wijbrieff, 1971). These antioxidants are normally associated with reactions of primary products of reaction of molecular oxygen with polymers, so the mode of action of this process is still uncertain.

W. R. Grace and Co. has applied for patents for the use of ascorbic acid dispersed into plastics such as the common heat-seal plastics or closure liners (Hofeldt and White, 1989). This process relies on the presence of water from the food or beverage as well as the presence of isoascorbic acid or a metallic sulfite such as sodium sulfite. The process is now commercial and follows the patent of Farrell and Tsai (1985) who patented the sandwiching of either a sulfite alone, or one mixed with potassium acetate, between the layers of a retortable pouch structure. Several other applications for oxygen-scavenging plastics containing ascorbic acid have subsequently been lodged. One combines oxygen scavenging with the antimicrobial action of a silver zeolite (Shinagawa Nenryo KK, 1992).

CMB Foodcan plc has developed a novel system for use in blow-moulded bottles made from PET into which up to 7% MXD-6 nylon had been blended (Cochran *et al.*, 1991). An additional catalyst in the form of a polymer-soluble cobalt salt such as cobalt stearate was necessary to cause the nylon to react with oxygen.

An example of the performance of a bottle made from the Ox-Bar (Trademark of CMB Technologies plc) has been given by Folland (1990). The results suggest that beer held in such a bottle would be saved from oxygen ingress via the bottle wall for at least 12 months thus providing oxygen-barrier performance functionally equivalent to that of glass. As with any form of active packaging, oxygen-scavenging plastics are designed to achieve a specific effect – in this case protection of a packaged food from oxygen. As it turns out, the shelf-life of carbonated beverages like beer is limited by the loss of carbon dioxide by permeation. Thus the effect of the oxygen-scavenging bottle would be to change the nature of the limiting

variable if used in those countries where beer has a high level of carbonation.

This process has not reached the market place since the reaction products need to be defined in greater detail. What is particularly interesting in this case is that the use of a cobalt salt catalyst in PET appears to have satisfied some national regulatory authorities.

4.2.4 Chemistry of oxygen scavenging

Unlike most other forms of active packaging, oxygen-scavenging films must be stable in the oxygen-rich environment of air prior to use. This has presented a problem to chemists formulating such systems and surprisingly few methods of activation appear either in the patent literature or in commercial practice.

In some instances activation might not be a necessary consideration if the package is prepared from all constituents immediately before filling. Such packaging systems would include blow-moulding of beverage bottles which often occurs on the premises of the beverage filler. Thus the catalyst and the oxidisable substrate can be kept apart until the bottle is blown, as in the Ox-Bar process developed by CMB Technologies plc.

A further factor is the nature of the packaging material carrying the oxygen scavenger. In the case of the PET bottle, containing MXD-6 nylon blended into the PET for instance, the oxygen permeability of the bottle is so low that a delay between blowing and closure is quite reasonable. A general guide to such circumstances is that if the plastic material actually carrying the oxygen scavenger is exposed to the outside air during its life as a package the system can probably be chosen not to have an additional activation step.

The systems which have been developed for use (or prospective use) in coatings, laminations or other plastics layers with high oxygen permeability are normally activated by one of the following mechanisms.

- Supplying a reagent on package filling, viz. hydrogen or water
- Supplying water as a solvent or swelling agent on filling.
- Continuous exposure to light as energy source.
- Brief exposure to light for activation of
 - chain reactions, e.g. autooxidation
 - rapid photoreduction of scavenger precursor

In each of the above processes several variants exist. For instance, the water can come from the food itself as described in the Oxyguard process of Toyo Saitan Kaisha Ltd, or in the variety of patents referred to in Chapter 1. This requirement is elaborated in the discussion on sachet technologies in Chapter

Water needed as a reaction solvent or to burst micro-capsules can be supplied from the retorting steam in the case of retortable plastics packages which are processed at around 120°C. In this case water vapour permeation can be sufficient from the outside of the pack as well as from the food itself and here heat is also a trigger for commencement of the process. Tsai and Wachel (1990) have shown that EVOH trays can take up as much as 2.8% extra water on retorting, and this diffuses out slowly over a period of some weeks.

4.2.4.1 Supplying a reagent. The oxidation of hydrogen by molecular oxygen requires metal catalysis at room temperature. Indeed such a process has long been used by microbiologists to generate low-oxygen-content environments for cultivation of anaerobic microorganisms. Conventionally a mixture of hydrogen (8%) in nitrogen is either flushed into the cultivation chamber or hydrogen is generated in a sealed anaerobic jar in the presence of an air headspace. The surface of palladium metal either as mesh or deposited on porous alumina catalyses the reaction to form water.

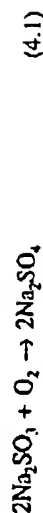
The application of this process to packaging by King (1955) and Abbott *et al.* (1961) was particularly successful for removing oxygen which desorbs from canned spray-dried milk powder. The hydrogen content of the flushing gas is limited to 7% or less to avoid the risk of explosion. It should be noted that an explosion limit of 6.5% hydrogen is specified in plants for production of chlorine by electrolysis.

The laminate bag described by Wambier and Wolf (1976) consists of a polyester outer layer bonded to aluminium foil then Surlin. Between this Surlin and the heat-seal layer, also of Surlin, is sandwiched a layer of powdered alumina upon which palladium metal has been deposited. The bag was flushed with the above-mentioned H_2/N_2 mixture before heat sealing. On storage the milk desorbed oxygen which diffused, together with the hydrogen, through the Surlin to react on the catalyst surface. The quantity of water which was formed was calculated by the authors to be insufficient to affect the food. There appears to have been very little use of this system, marketed as Maraflex 7F by American Can Company, with foods although it was used in the US space programme.

The oxidation of iron in the presence of electrolytes has been well established in the sachet technologies reviewed in Chapter 6. Where patents describe incorporation of treated iron powder into plastics, water ingress is generally needed. Some specify the need for such materials to be used under retorting conditions. This is probably for the purpose of introducing sufficient water on to the iron surface to carry out the reactions described in Chapter 6. It is doubtful whether an adequate rate of oxygen scavenging can be achieved when the polyolefin heat-seal plastics are used as the reaction medium at room temperature.

4.2.4.2 Supplying water as a solvent or swelling agent. Some packaging applications potentially permit the use of scavenging components as heterogeneous additives to the packaging material. Particularly where reagents are in the crystalline form or coated with a low-permeability substance, the rate of reaction with atmospheric oxygen can be acceptably low for incorporation into packaging. When the package is exposed to high humidity and elevated temperatures the rate of transmission of water from either the food or the outside (e.g. as steam) can be sufficient to dissolve the reagent thus enabling oxidation to proceed rapidly.

An early example of the dissolution of a salt was patented by Farrell and Tsai (1985). They incorporated a mixture of potassium acetate and sodium sulfite crystals (or potassium sulfite alone) between the barrier and heat-seal layers of a retort pouch laminate which had five layers overall. The potassium acetate is deliquescent and absorbs sufficient water to dissolve when the food-filled pouch is retorted. The sodium sulfite dissolves in the potassium acetate solution and reacts with oxygen diffusing into this solution from the food and especially from the retort atmosphere. The water vapour permeability of the laminate can increase 1000-fold from 21°C to 121°C. The sulphite reacts with oxygen as in Equation 4.1.



Although this process can result in the presence of an aqueous solution in the laminate, it should be possible to consider use of some form of binder for the solution after retorting. A process such as this which requires both heat and high humidity is really limited to applications which involve retorting or substantial heat-treatment of the packaged food.

A recent patent describes the incorporation of a metallic salt and a complexation agent in separate microcapsules within a polymer film (Zenner *et al.*, 1992). On exposure of the film to an atmosphere of high relative humidity, as in the headspace of some food packs, the microcapsules absorb water and swell. This results in bursting of the microcapsules and mixing of the complexing agent and the salt under moist conditions. The resultant metal chelate forms an oxygen adduct with a binding constant greater than $10^9 M^{-1}$. The presence of such a strong adduct is effectively equivalent to oxygen removal by means of an irreversible reaction.

The reaction of oxygen with a metal complex can also involve a weak coordinate bond without converting the metal ion to a higher oxidation state. This type of reaction is the basis of blood oxygenation and can frequently be reversed, at least to some extent (see Chapter 1). This type of oxygen absorber was the subject of extensive research by Aquanautics Inc in the USA, the predecessor of Advanced Oxygen Technologies Inc.

Ascorbic acid and isoscorbic acid react readily with oxygen, more rapidly at high pH. The use of metallic salts of these acids is described in

patents from many sources. The chemistry of oxidation of ascorbic acid is complex, consisting of a series of consecutive and concurrent reactions, depending upon the conditions. The steps involved in the commercially accepted scavenging compositions have not been described in the scientific literature. It has been observed in the author's laboratory that cellulose acetate films containing dissolved ascorbic acid turn light-brown in colour after standing in darkness under ambient temperature and humidity conditions for one to two years.

The steps involved in ascorbic acid oxidation in solution have been reviewed by Tannenbaum (1976) who summarised the reactions involved in the oxidation of ascorbic acid. A simpler summary is shown in Figure 4.2. The initial step is the formation of dehydroascorbic acid and this step is strongly dependent upon pH. Ascorbic acid can be regenerated by reaction with mild reducing agents such as metallic sulfites. It is particularly interesting that the patent of HofeKit and White (1989) describes the optional use of sodium sulfite in combination with ascorbic acid (and its isomers) in their oxygen-scavenging closure liner for use with beverages such as beer. There is thus the potential for use of ascorbic acid as an intermediate in the

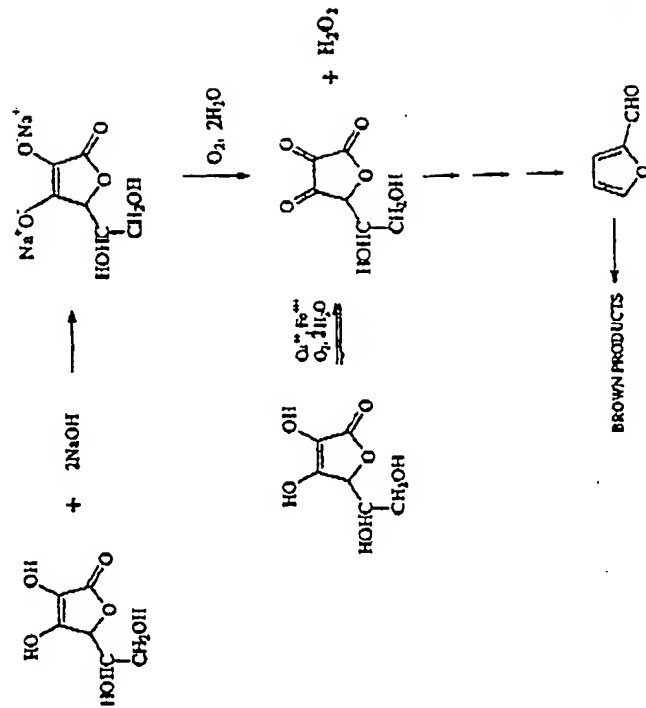


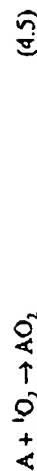
Figure 4.2 Oxidation of ascorbic acid.

oxidation of sodium sulfite to the sulfate. Whether this occurs in the ambient or low-temperature storage of beer has not been described in the literature. Given the heterogeneous nature of the reaction mixture it is doubtful whether this desirable regeneration occurs to a very great extent in commercial practice without the formation of an aqueous solution as described by Farrell and Tsai (1985).

As can be seen from the summary in Figure 4.2 one of the reaction products of oxidation of ascorbic acid to dehydroascorbic acid is hydrogen peroxide or initially the hydroperoxy free radical. Further hydrogen abstraction by this radical forms hydrogen peroxide. The use of sodium sulfite, or another reducing agent, would therefore seem to be desirable if the ultimate re-introduction of an oxidising agent is to be avoided. The role of ascorbic acid as a promoter of browning when oxidised in foods is already known (Tannenbaum, 1976).

The use of ascorbic acid or its isomers or salts is the basis of the W.R. Grace and Co. and Zapata Inc oxygen-scavenging closures in common use in some beer bottles.

4.2.4.3 Continuous exposure to light as an energy source. Some oxidation reactions which do not occur when oxygen is in its unexcited (ground) state can be brought about by the process of photosensitisation, which involves transfer of visible light energy to oxygen via the intermediacy of a dye. A polymer film can be the medium for these photosensitised oxygen-scavenging reactions. Such a film must contain a photosensitising dye and an electron-rich oxidisable compound termed a singlet oxygen acceptor. The oxygen-scavenging process occurs when the film is illuminated with UV, visible or near infra-red irradiation of appropriate wavelengths. The steps in the process are shown below, and these occur within the matrix of the polymer film.



When a suitable photosensitiser, D, absorbs light ($h\nu$) it is excited to a short-lived higher energy singlet state, 1D , (Equation 4.2) which largely converts to the longer-lived triplet excited state, 3D , (Equation 4.3). In this form the dye can pass the excitation to oxygen by the process of triplet-

triplet energy transfer (Equation 4.4). The oxygen diffusing into the polymer from the package headspace (for instance) needs to come very close to the excited, immobile dye molecules during the triplet lifetime of the latter. This is of the order of 10–1000 microseconds. Thus, for such a process to be useful the polymer matrix (such as an inner layer of a laminate) would need to be very permeable to oxygen.

Once excited to its singlet state the oxygen can react with any electron-rich acceptors, A, present in the polymer matrix (Equation 4.5) provided they are within the distance the singlet oxygen can diffuse before it is quenched back to the ground state (Equation 4.6). The process occurs only within the lifetimes of the excited sensitizer (Equation 4.7) and singlet oxygen and so requires continuous illumination. The distance singlet oxygen can diffuse before quenching in a polymer matrix is of the order of 100 Å depending on the polymer permeability and other factors (Turro *et al.*, 1981).

This chemistry has been used in the laboratory as an oxygen-scavenging process where the polymer matrix is, for instance, cellulose acetate or ethyl cellulose (Rooney *et al.*, 1981; Rooney, 1982). The sensitizers include erythrosine or *meso*-tetraphenylporphine and the acceptors are bis(furylidene)pentacrythritol and ascorbic acid. It was found that the permeability of the polymer film is an important determinant of scavenging rate, with the ethyl cellulose being a better matrix for rapid scavenging than cellulose acetate. Ethyl cellulose has an oxygen permeability coefficient at 25°C of 7 Barrers ($\text{cm}^3 \text{ (STP) cm/cm}^2 \text{ s}^{-1} \text{ Hg} \times 10^{-10}$) compared with that of 0.7 Barrers for cellulose acetate (Bixler, 1971). It was also found that the rate of scavenging of oxygen from a pouch by the film is limited by light intensity initially but becomes diffusion limited when the oxygen partial pressure reaches low values (Rooney *et al.*, 1981). The light intensity used was 2×10^5 – 7×10^5 Lux. It was subsequently shown that the rate of oxygen scavenging reaches a maximum at a concentration of tetraphenylporphine above 10^{-3} M but less than 10^{-2} M. When the scavenger film was used as a roll it was found that the rate was dependent upon the length of film in the roll consistent with increased access of oxygen to the film.

The singlet oxygen acceptor does not need to be a small molecule dissolved in the polymer. It has been shown the double bond of natural rubber can be photo-oxidised at a rate sufficient to bring about rapid oxygen scavenging from the headspace of a package. Figure 4.3 shows the rate of scavenging of oxygen from air, 20 ml, in a 10 cm \times 10 cm pouch coated on the inside with either natural rubber dyed with tetraphenylporphine, 10^{-3} M, or ethyl cellulose 0.6 M with respect to PEF and 10^{-3} M with respect to tetraphenylporphine. The rubber scavenged oxygen substantially faster than the PEF in the ethyl cellulose. This was interpreted as being due to the higher concentration of double bond (13.5 equivalents/litre) in the rubber than the concentration of furan rings (1.2 equivalents/litre of film) in the

(bifunctional) PEF, although the higher permeability of rubber towards oxygen (24 Barrers) than that of ethyl cellulose (7 Barrers) is also likely to contribute. It is significant that the reaction occurring in natural rubber occurs on the polymer chain and therefore is not dependent on the free rotation of the acceptor. The photo-oxidation of the tacky natural rubber layer resulted in rapid crosslinking as indicated by the loss of tack within minutes. An unpleasant odour was also generated. The oxidation of the rubber continued on dark storage resulting in formation of a brittle powdery film.

The potential for use of synthetic rubbers in place of natural rubber was investigated in order to determine whether the nature of the rubber monomers affects the rate of scavenging. The results in Figure 4.4 show the rate of oxygen scavenging by poly(dimethylbutadiene) (PDMB), *cis*-polybutadiene (PB) and *cis*-polyisoprene (PI). Based on the reactivity of simple low-molecular weight analogues of these polymers, it would be expected that the more highly methylated rubber poly(dimethylbutadiene) would react more rapidly with singlet oxygen. However, the inverse relationship is observed, presumably due to the low oxygen permeability of PDMB of 2.1 Barrers compared with values of 20 Barrers and 24 Barrers for PB and PI. Thus permeability rather than reactivity can be the important

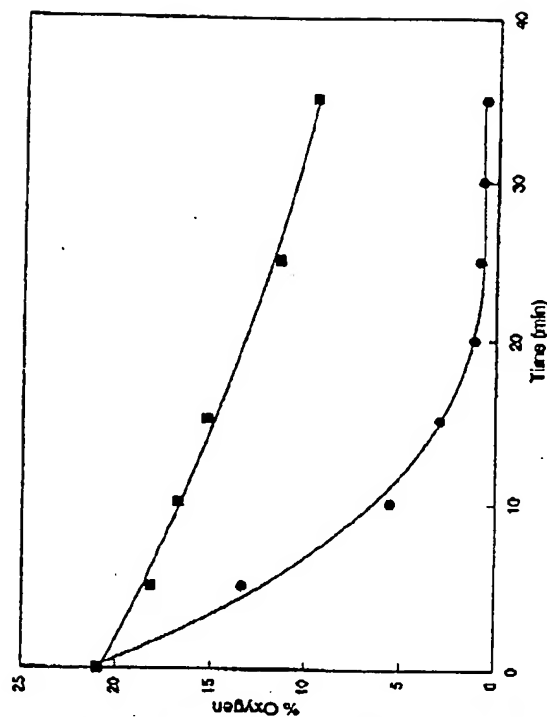


Figure 4.3 Oxygen scavenging by natural rubber \bullet and PEF 0.5M in ethyl cellulose \blacksquare , both dyed with tetraphenylporphine, 10^{-3} M. Volume of air, 20 ml, pouch area 100 cm^2 . (Reprinted from Rooney, 1982b, with permission.)

4.2.4.4 Brief exposure to light for activation

4.2.4.4.1 Chain reactions. Continuous exposure of a package to light places an intolerable restriction on the way in which most foods would need to be stored and distributed. It is not surprising therefore that the use of light to activate reactive polymer-based systems has been investigated. The problem, inherent in all oxygen-scavenging systems, of using compounds reactive towards oxygen but stable towards thermal processing of the packaging material needs to be addressed.

The use of autooxidation of fatty acids for oxygen scavenging has already been claimed but this process seems likely to result in formation of the same volatile oxidation products which are undesirable in foods (Frankel, 1982). Some sachet patent applications describe the use of adsorbents in the sachets to bind volatile off-flavours generated in this way. Mitsubishi Gas and Chemical Company has claimed that activated alumina, silica gel or charcoal absorbs any odour formed on the oxidation of fatty acids or oils catalysed by transition metal compounds in the presence of alkaline earth bases (Inoue and Komatsu, 1988). Toppan Printing Company (1992) claimed a similar composition involving addition of activated clay. The benefit of such systems is independence from water for the reaction. The benefit of such into development of photodegradable plastics packaging over the past two decades has provided a background to one approach to this problem.

Rabek and Ranby (1975) show how a transition-metal metal salt and a photosensitiser dispersed in a plastic can cause it to degrade in darkness once exposed to sunlight for some days. This form of photodegradation involves a substantial extent of hydrogen abstraction from the polymer backbone coupled with hydroperoxide formation, particularly on tertiary carbon atoms. Subsequent breakage of the hydroperoxy bond leads to formation of either keto or aldehyde groups which become additional photosensitisers or result in polymer chain scission. It is in the prevention of the latter reaction that the opportunity for development of oxygen-scavenging polymers exists.

The scavenging of oxygen including oxidation of hydrocarbon polymers impregnated with salts of transition metals has been described by Speer *et al.* (1993). The novelty of their method is that the oxidation process is activated by brief exposure to light of wavelengths less than 750 nm. The optional use of a photosensitiser is reported to increase the rate of activation, particularly in the presence of an antioxidant.

As with the photodegradable plastics processes, the chemistry involves initiation of the free radical process on the polymer chains by changes in the oxidation state of the transition metal ion, preferably cobalt. The redox reaction on the polymer chain involves either hydrogen abstraction in polypropylene or polyethylene or oxygen attack on the double bond in the case of poly(1,2-butadiene).

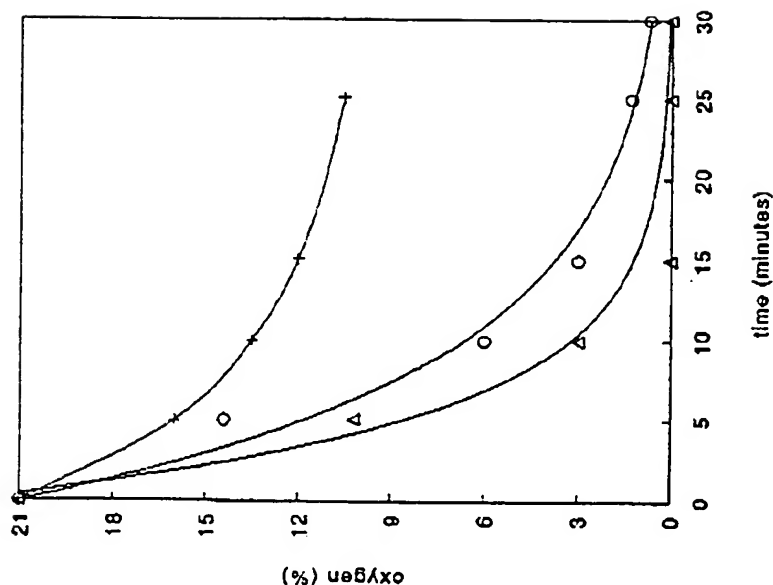


Figure 4.4 Oxygen scavenging by polydienes, poly(1,2-butadiene) ×, cis-polyisoprene O, polybutadiene Δ. Coatings on inner surface of pouches of area 100 cm², volume of air 20 ml.

variable in an oxygen-scavenging polymer system as was found to be the case with PEF dissolved in cellulose acetate and ethyl cellulose.

The use of multiple dyes in oxygen-scavenging films has been investigated, since illumination with white light of polymer films containing only one dye is wasteful of potentially usable energy (Rooney *et al.*, 1994). It has been found that even dyes which are not photosensitisers can harvest energy and transfer this energy to a photosensitiser also in the film. Thus curcumin, a natural food colour and a poor photosensitiser (Chignell *et al.*, 1994), was shown to enhance the rate of oxygen scavenging photosensitised by eosine in ethyl cellulose. The effectiveness of such a film in suppressing rancidity in sunflower oil has been investigated and found to be substantial at 23°C and 37°C (Maloba *et al.*, 1994).

The hydroperoxide formed by reaction of either the polymer free radical or by direct attack on the polymer decomposes to form ketones, aldehydes, peroxides or carboxylic acids, in some cases with chain scission. In the case of poly(1,2-butadiene) it is the aim to localise the oxidation to the side chain containing the double bond. Speer *et al.* (1993) report that this polymer retains its physical properties even when most or all of its oxidisable groups have been reacted. Since this is a typical autooxidation that is also thermally activated, the polymer needs to be stabilised against premature initiation in the extruder or moulding machine in package fabrication. Antioxidants provide this protection. The quantity of antioxidant is chosen both to provide this protection and to retard the autooxidation chain reaction for a selected period of time between activation and package filling. Removal of antioxidant from the polymer appears likely to increase the likelihood of taint formation due to unrestricted polymer oxidation. Attention should probably be given to inclusion of odour absorbents in the composition as proposed by Toppan (1992).

The manner in which such a system could be used is particularly broad but one suggested is to laminate or coextrude the reactive layer with an oxygen-barrier layer. Such an application would be appropriate for many packaging processes such as in the storage of cheese, nuts and meats such as beef primal cuts.

The use of such compositions at the low temperatures required for storage of meats and cheese requires that the reactive layer be readily permeable to oxygen. Speer and Roberts (1993) have specified that the compositions containing their oxidisable components should be largely amorphous and have a glass transition temperature below -15°C .

4.2.4.2 Rapid photoreduction of a scavenger precursor. Research into systems involving this form of triggering indicate that this approach overcomes some of the limitations of other methods already proposed (Rooney, unpublished results).

4.2.5 Chemical barrier to oxygen permeation

Implicit in the use of oxygen scavenging inserts (sachets) or closures is the effect these have on the consumption of oxygen as it enters the product during its storage life. The results in Table 4.5 show the calculated impact of

Table 4.5 Calculated life of chemical oxygen barriers

Film	OTR $\text{cm}^3 \text{m}^{-2} \text{day}^{-1} \text{atm}^{-1}$	Barrier life (days)
LDPE 25 μm	8000	< 1
PET 25 μm /LDPE 25 μm	63	56
PVDC-coated OPP 25 μm	9	362
Metallised PET 12 μm /LDPE 25 μm	0.5	7250

the oxygen transmission rate of packaging materials on the period of effective oxygen scavenging by a commercial oxygen-scavenging sachet with an absorption capacity of 50 ml of oxygen. The packages are $10 \text{ cm} \times 20 \text{ cm}$ and initially contain 100 ml air. LDPE is low-density polyethylene, OPP is oriented polypropylene, PET is polyester and PVDC is poly(vinylidene chloride). However, in a food-packaging situation where the food is tightly packed, the sachet can be expected to deoxygenate only a small portion of the headspace and combat permeation of oxygen that is accessible to it.

Close-fitting packages such as vacuum packs for block cheese and meats or aseptic cartons of beverages are examples where the headspace is very small and oxygen permeation is the prime cause of quality loss. It is in such circumstances that oxygen-scavenging plastics films are particularly needed. The use of the oxygen-scavenging reaction to intercept oxygen diffusing through the package wall is an example of a chemical barrier as distinct from the physical barrier normally provided by aluminium foil and vacuum metallising or crystalline polymers such as poly(vinylidene chloride).

The use of a chemical oxygen barrier offers the opportunity to cheapen barrier packaging for relatively short shelf-life products such as wholesale or export units or for some fresh foods. This can be achieved by using a barrier film of intermediate performance coupled with a chemical barrier. This combination was investigated by Rooney and Holland (1979) and the results in Figure 4.5 demonstrate a period of total barrier to oxygen permeation from air at 25°C . A laminate of polyethylene/nylon α /cellulose acetate containing oxygen-scavenging reagents was used to separate the two compartments of a glass permeability cell. When the ethyl cellulose layer contained 0.5 M bis-furfurylidene-penterythritol, illumination with fluorescent light resulting in a barrier life of around 30 days was followed by a period of oxygen transmission at a rate less than that found in darkness. In this case the chemistry used was a singlet oxygen reaction which requires constant illumination to photo-excite the oxygen. Other chemistries can be used to achieve similar reactions in darkness and Speer *et al.* (1993) identified this application for their photoinitiated chain reactions in rubbers, and Cochran *et al.* (1990) devised the Ox-Bar process largely for this purpose.

The use of oxygen-scavenging sachets to allow the use of a cheaper packaging material has been described by Alarcon and Hotchkiss (1993) and their work is reviewed in Chapter 6.

Although use of multilayers of plastics films appears the most appropriate approach to solving permeability problems, there have been early attempts to carry out scavenging reactions in liquid layers. Oxygen scavenging in liquid layers was one of the earliest processes described in the patent literature. Cook (1969) claimed that bilayers of plastics films separated by a layer of a solution of one of several antioxidants in high boiling point solvents

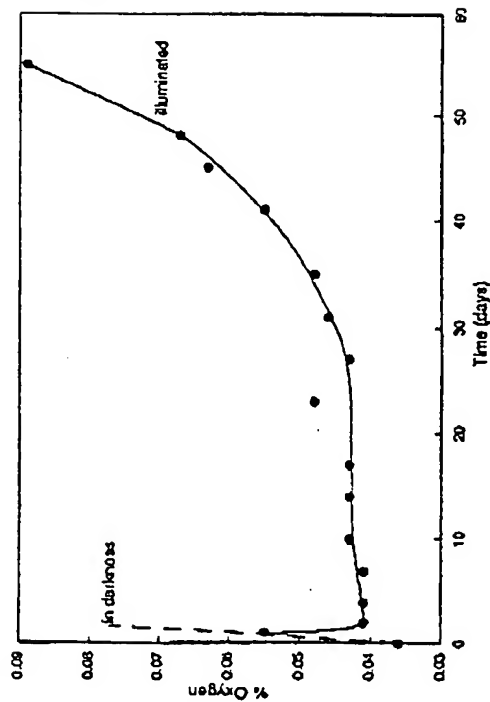


Figure 4.5 Barrier to oxygen permeation of polyethylene/Nylon 6/cellulose acetate laminate. Cellulose acetate 26 μ m thick containing PEF (0.5 wt) and erythrosine, 5×10^{-4} M. Oxygen concentration measured in a cell on the cellulose acetate side of the laminate, air on the other side.

demonstrated a reduced oxygen permeability. Whereas the mechanism was unknown, all of the common antioxidant classes were claimed to be effective.

Use of an aqueous solution of an oxygen-scavenging reducing sulfite as a layer between two polymeric layers has been claimed by Scholle (1976). As with the organic system of Cook (1969), the purpose was to reduce the oxygen permeability of the laminate. In the case of Cook's system the role appears to have been to improve shrinkable packaging, as for meat, whereas the Scholle system was particularly suitable for bag-in-box liners since the packages consist of, at least, a collapsible duplex which is sealed together only at the edges where the liner forms a bag (and around the tap filling). Such a system requires an oxygen scavenger for oxygen-sensitive products due to the gas space between the two film layers.

4.3 Moisture control films

Moisture affects the gas and vapour permeability of hydrophilic plastics packaging films (Davis, 1966). Fruit cakes packed in films with an appropriate water vapour permeability can have long shelf-lives because the surface dries somewhat. This creates conditions unfavourable to mould growth. Nitrocellulose-coated regenerated cellulose has been used because it

prevents contamination with moulds and allows substantial water vapour permeation.

There are, however, several sets of circumstances in food packaging where greater selectivity in control of liquid and gaseous water is required. These include:

- Transpiration of horticultural produce.
- Melting of ice, e.g. in fish transportation.
- Temperature fluctuation in high erth food packs.
- Drip of tissue fluid from cut meats and produce.

The problems which arise from these circumstances are the result of build-up of liquid water. Alternatively, the natural water level in the tissue can be undesirably high near the surface for microbiological stability under the chosen storage conditions. The results of the presence of water in unwanted quantities include bacterial (yeast) and mould growth as well as fogging of films and mobile blood and tissue fluid. Moisture migration via the vapour phase can result in transient formation of regions without adequate preservative or where the a_w is high even though the food is packed at lower a_w . Some of the ways of addressing these problems via packaging are considered in detail in terms of either liquid water control or humidity buffering.

4.3.1 Liquid water control

Temperature cycling of high erth foods has led most film manufacturers to use heat-seal plastics with anti-fog additive. These additives are blended with the resin before extrusion and migrate to the surface after film formation. The additives are chosen for their amphiphilic nature with the non-polar chain in the plastic and the polar end group at the interface. The result is a lowering of the interfacial tension between water condensate and the plastic film. The fog droplets therefore coalesce and form a transparent film on the plastic. This film may even flow on sloped surfaces and gather at the bottom of the pack in extreme circumstances.

Anti-fog treatments are a cosmetic form of active packaging, assisting the customer to see the packaged food clearly. There is no change in the availability of liquid water in the package and this has the potential to cause produce spoilage unless managed by one of the processes described below. Other active packaging systems go further in removing liquid water from food contact.

Several companies manufacture drip-absorbent sheets, which may have a variety of other names. Basically they consist of two layers of a microporous or non-woven polymer, such as polyethylene or polypropylene, between which is placed a superabsorbent polymer in the form of free-flowing granules. The duplex sheet is sealed at the edges and is normally quilted to

allow the water absorbent to be held in place rather than aggregating towards one edge of the sheet when tilted towards one edge.

Such sheets are then used either as pads under whole chickens or chicken pieces to absorb drip, thereby preventing discoloration of either the meat or the white foam tray. Given the interest in reducing the volume of solid waste by decreasing foam polystyrene usage, the use of drip-absorbers may become even more necessary to prevent water damage to the more hydrophilic alternatives.

Large sheets are used for absorption of melted ice in the packaging of seafood for air transportation. The superabsorbent polymer used in the Thermaite® Pty Ltd sheet manufactured in Australia is capable of absorbing at least 100 times and possibly as much as 500 times its own weight of liquid water depending dramatically upon salinity (Malouthi *et al.*, 1994). Another product of this type is Toppan Sheet manufactured in Japan. A recent patent application in Japan describes a water-absorbent sheet which has a high barrier to oxygen for use with fresh meat (Showa Denko KK, 1990). This would necessitate use of a sealed outer pack.

The preferred polymers used to absorb the water are polyacrylate salts, although graft copolymers of starch can also be used. Such copolymers consist of a polysaccharide backbone with synthetic polymer chains radiating from the starch backbone. The strong association of the polysaccharide chains is disrupted allowing the starch to exercise its affinity for water by hydrogen bonding. Such polymers tend to become slimy when swollen with large amounts of water.

The swelling of the polymer on hydration results in substantial distortion of the duplex sheet, an effect that is controlled somewhat by the quilted seal pattern. This effect can be controlled by choice of the amount and the capacity of the superabsorbent polymer.

The significance of such active packaging in seafood shipment by air lies in the removal of the potential for spillage of salt water from cartons in aircraft holds. The aluminium construction of aircraft makes them easily susceptible to corrosion damage, at great cost.

4.1.2 Humidity buffering

An entirely different approach to the control of excess moisture in food packages is to intercept the moisture in the vapour phase. This approach allows the food packer or even the householder to reduce the surface concentration of water in a food by reducing the in-pack relative humidity. This can be done by placing one or more humectants between two layers of a plastic film which is highly permeable to water vapour. An example of this type of product is Pichit manufactured by Showa Denko in Japan. The film duplex is described as containing an alcohol, described by Labuza (1989) as propylene glycol and a carbohydrate, both of which are humectants.

Table 4.6 Water vapour uptake by Pichit and Toppan sheet

Time (h)	Weight loss from petri dish (%)	
	Pichit	Toppan sheet
2	1.2	-
3	2.4	0.7
4	3.6	1.2
24	15.2	8.4
26	22.0	8.8

The effectiveness of such a combination material in comparison with a superabsorbent polymer absorbent for liquid water is shown in Table 4.6. Distilled water 5 g was placed in each of two petri dishes (with lids) and these were enclosed with either Pichit or Toppan Sheet (450 cm²) in a high-barrier package. The packages were opened at intervals and the petri dishes were weighed to give the per cent loss of weight of water, shown in Table 4.6. Thus, whereas the superabsorbent polymer has a far greater capacity for liquid water uptake, the humectant-based film more rapidly absorbs water vapour.

Pichit is marketed for home use in roll or single sheet form for wrapping pieces of fresh food such as fish or chicken to reduce the a_w proximate to the food. At present there is a lack of experimental verification of the significance of this effect. Louis and de Leiris (1991) suggest two to three days of fresh storage is possible. It has been suggested by Labuza (1989) that the permeability of poly(vinyl alcohol) to propylene glycol may be sufficient to allow some of the latter to diffuse to the food surface. If this is the case, some antimicrobial action might be expected. Propylene glycol is a GRAS substance in the USA.

Louis (1991) reports the availability of an additional moisture control film which plays the same role as Pichit in the Japanese market. The potential for use of such materials for quality retention in the home appears to be considerable and this type of film should be subjected to detailed objective evaluation for use in the domestic situation where excess portions of fresh foods need refrigerated storage for some days. The potential for washing the surfaces of sheets like Pichit, followed by re-use, is an attractive incentive for active packaging use in the home provided absence of microbial contamination can be demonstrated.

A different approach to humidity buffering has been under investigation for use in the distribution of horticultural produce. Currently the packages are wholesale fibreboard cartons of produce, usually with a polyethylene liner or consisting of the very expensive waxed fibreboard without a liner. A recent development has been the water-barrier coating of the inside of fibreboard cartons to allow moist produce to be placed directly into the carton. Besides the introduction of liquid water with the produce, packing into closed spaces allows the build-up of water vapour. The produce

continues to lose water by evaporation during distribution and the relative humidity in the lined carton can reach close to 100%. Since temperature cycling is very difficult to avoid during handling, there is every likelihood of condensation, and, with this, the growth of microorganisms on fruits and vegetables.

Two widely different approaches have been taken to buffering the humidity in the cartons in order to prevent condensation while not concurrently causing desiccation of the produce. One is to include microporous bags or pads of inorganic salts and the other is to line the carton with a protected layer of a solid polymeric humectant.

The approach of using microporous sachets of inorganic salts has been used in the US tomato market in recent years. This was proposed by Shirazi and Cameron (1992) who showed that an equilibrium relative humidity of around 95% above produce can be reduced to around 80% by use of sachets of desiccant salt such as sodium chloride. The application was extended by Hudson (1991). Both these studies involved use of heat-sealed liners which were concurrently being evaluated for their performance to maintain equilibrium modified atmospheres (EMA) generated by the fruit (see Chapter 3). The control of moisture is one of the main impediments to the introduction of EMA packaging. Indeed it is common to package potatoes in perforated sacks to prevent unwanted build-up of condensation.

The most recent alternative involves the use of the carton as the active package rather than an insert. This approach lends itself to combination with EMA generation less readily as the humidity is buffered at the interface with the fibreboard. The designs of Patterson and Joyce (1993) involve: an integral water vapour barrier layer on the inner surface of the fibreboard; a paper-like material bonded to the barrier and which acts as a wick; and a layer highly permeable to water vapour but unwettable next to the fruit or vegetable. The latter layer is spot welded to the layer underneath. Accordingly, the multilayer of material on the inside of the carton is able to take up water in the vapour state when the temperature drops and the RH rises. When the temperature rises the multilayer releases water vapour back into the carton in response to a lowering of the RH. The condensation control system therefore acts as an internal water buffer. The critical characteristic of the system is the capacity of the wick layer for water.

The performance of this system is demonstrated in Table 4.7 taken from Patterson *et al.* (1993) which shows the results of a comparison of the free

Table 4.7 Free water in carrot packs on cooling

Packaging	Cooled from 10 to 3°C	Cooled from 22 to 3°C
Polyethylene liner	10.1 (0.6)*	22.9 (0.7)*
Condensation control carton	0.0 (0.0)*	0.2 (0.2)*

*Standard error of the means ($n = 5$)

water found in cartons of carrots with a conventional liner with the condensation control multilayer. The cartons containing carrots, 6 kg, were cooled to 3°C from either 10°C or 22°C and after 3 days the amount of free water in the boxes and on the carrots was measured. The results demonstrate the capacity of such a system for water uptake under circumstances likely to be found in commerce.

Shrink wrapping is an alternative approach to the use of active packaging systems for control of condensation on spherical fruits such as citrus. Ben-Yehoshua (1989) has reviewed this field, to which he has made such a large contribution.

4.4 Removal of taints and food constituents

The interaction of packaging plastics with food aroma has long been recognised, especially through the flavour 'scalping' which is of considerable commercial interest. Hirose *et al.* (1989) demonstrated the impact of the nature of the metal ion in Surlyn film layers in aseptic brick-packs on the scalping of limonene from orange juice. In periods as short as 2 weeks at 24°C, almost 30% of the limonene was found in the Surlyn-1601 and 20% in the polyethylene layer in brick packs. Commercially, plastics packaging has not been used to remove selectively components of the flavour or aroma of foods which are considered undesirable, but a potential opportunity has been available for over a decade.

Some varieties of orange, such as the Navel, contain a tetraterpenoid of the formula $C_{28}H_{46}O_4$ which is initially present in the albedo but which is extracted into the juice on standing or heating. Thus the juice of such oranges becomes bitter on pasteurisation when this compound, limonin, reaches concentrations exceeding 8–12 mg/kg (Chandler *et al.*, 1968). Processes have been developed for detainting such juices by passing them through columns packed with cellulose triacetate or nylon beads (Chandler and Johnson, 1979).

A simple active packaging process was suggested by the same authors, who proposed that since the juice extracts the bitter principle on standing for 24 h, inclusion of the absorbent in the packaging might remove it as it is extracted. To this end they proposed using their absorbents in film form such as cellulose triacetate or as acetylated paper. They showed that a 1-litre plastic bottle coated internally with cellulose acetate-butyrate reduced the limonin content of 500 ml of juice from 42 to 11 mg/kg after 3 days' refrigeration. Similarly, when cans lined with acetylated filter paper containing juice with 14.9 mg/kg limonin were spin cooked and allowed to stand, the juice was only slightly bitter after 4–13 days.

It appears that this process has not been taken up commercially although it offers considerable potential for freshly squeezed Navel juice marketing

(Johnson, R.L., private communication). On the other hand, the sorption of limonene oil from packaged juices by heat-seal layers has been the subject of several studies (Mannheim *et al.*, 1989; Hirose *et al.*, 1989). Thus opportunities for active packaging can be closely related to problems of food-package interactions.

A closely related goal had long been achievable commercially in the tinplate canning of foods in which protein degradation resulted in the release of sulfur compounds from the food. These sulfur compounds cause the phenomenon of 'sulfur staining' on the tinplate and so it has been the practice to disperse zinc oxide in tinplate lacquers to intercept such compounds reacting with them before they can diffuse to the tinplate surface.

The remaining methods described in the literature to date for removal of taints or off-flavours have largely involved incorporation of ingredients with a specific interaction or reaction with a functional group known to be present in the taint or undesirable food component. Two types of taints amenable to removal by active packaging have been identified by researchers responsible for current commercial products. These are amines resulting from protein breakdown in fish muscle and aldehydes formed from the breakdown of peroxides which result from the initial stages of autooxidation of fats and oils. The formation of aldehydes can make a wide variety of oil-containing foods organoleptically unacceptable well before there is significant damage to the nutritional or functional properties of the food. Examples of such products would be fried snackfoods such as potato crisps, biscuits and cereal products. Early developments occurred in Japan where there was seen to be a need to remove amine smells from fish which was stored in domestic refrigerators. The amines formed in fish muscle degradation include strongly basic compounds and thus are potentially strong in their interaction with acidic compounds such as citric or other food acids. Hence the earliest work involved incorporation of such acids in heat-seal polymers such as polyethylene and extruding them as layers in packaging (Hoshino and Otsuai, 1986).

A later approach to removal of amines odours has been provided by the ANICO Company Ltd in Japan under the trade name ANICO BAG. Bags made from film containing ferrous salt and an organic acid such as citric or ascorbic acid are claimed to oxidise the amine or other oxidisable compound as it is absorbed by the polymer.

If these materials can be shown to be effective there is an opportunity to determine which variables optimise their rate and extent of reaction. Questions which would need to be answered are What is the nature of the products of such reaction and What is their fate. Questions such as these are of particular interest to regulatory authorities, and the potential for several active packaging systems to generate mobile reaction products is considered in Chapter 11.

Removal of aldehydes such as hexanal and heptanal from package headspaces is claimed by Dupont Polymers, Packaging Division, for their recently introduced tie layer Bynel IXP101 which is a high-density polyethylene (HDPE) resin masterbatch. This masterbatch is blended (2.5–12%) with unmodified HDPE or other linear polyethylenes to form an intermediate layer in coextrusions. It is specified that the heat-seal layer should not be a 'good to excellent gas barrier' (Dupont, 1993). It is interesting to note that the use of a form of active packaging can place restrictions on other components of the packaging. The restriction in this case, and many others, is that the extrusion temperature should not exceed 220°C to avoid fuming. The chemistry of the process is not described but such a process would require the reaction with the aldehyde to be effectively irreversible at least over the temperature range the package is likely to encounter. One such reaction would be the formation of a Schiff base by reaction of the aldehyde with an amino group. The amino group would need to be rather stable to heat and oxygen in order to remain unaffected after the extrusion at temperatures up to 220°C in an air atmosphere.

There may well be a wide range of food constituents which can be removed by making use of specific interactions with selected packaging components or by chemical reaction with them. A fertile research field would seem to be open especially with liquid foods since solubility and diffusion of food constituents in the packaging can be utilised so that the removal process is not limited to compounds with a significant vapour pressure at distribution temperatures. It will be necessary for industry and regulators to ensure that such processes are not used to conceal the marketing of sub-standard or even dangerous products if for instance microbial odours were to be scavenged.

The tainting of foods by compounds originating either in the packaging material itself (e.g. monomers) or outside but permeating the packaging material continues to be a source of problems for the food industry. The approaches described above may contribute to their solution but additional approaches have been described in the patent literature. These are formation of chemical barriers as distinct from physical barriers like aluminium foil or crystalline polymers.

Myrcene (7-methyl-3-methylene-1,6-octadiene) has been found to react with traces of styrene or acrylonitrile when the latter are present in acrylonitrile-butadiene-styrene copolymers or blends being extruded (Tolks, 1979). Addition of myrcene is claimed to introduce no new taint while reducing residual levels of the monomers. In another patent, foods packaged in plastics consisting of more than one layer are claimed to be protected against taints from the outside by inclusion of the appropriate adsorbent in the outer layer (Kiru Kogyo KK, 1994). The adsorbent is chosen for expected taints and is kneaded onto the outer layer, apparently retaining the taints there. The period of this type of equilibrium adsorption

needs to be established, especially when a package is subjected to temperature changes. This may have application in areas where products are to be stored or shipped together with odorous products which are inadequately packaged.

A compound which while not a taint is often found undesirable in packages of respiring horticultural produce is the gaseous auxin ethylene. The potential benefits resulting from such removal are particularly great and are discussed separately in Chapter 2.

4.5 Ingredient release

Active packaging materials considered so far have exerted their action on the packaged food by removing unwanted components of either the food or of the headspace enclosed with the food. Another form of interaction is by release of desirable ingredients into the food from the packaging materials or from inserts packaged with the food. Some substances released commercially or which have been the subject of investigation are listed in Table 4.8. Most are used for their antimicrobial activity, although sulfur dioxide also serves as a chemical stabiliser of colour and flavour by preventing progress of the Maillard reaction which causes non-enzymic browning of products such as dried fruit and wines (Davis, 1975; Davis *et al.*, 1978). Hinokimol, also known as β -thujapricin (Iirata, 1992), derived from cypress bark, is an additional antimicrobial compound specific to the Japan market.

Processing of foods often results in loss of flavour by degradation or evaporation. Another mechanism of flavour loss is the scalping of some flavour components by plastics used in packaging (Mannheim *et al.*, 1989). There is therefore the opportunity to replace these lost food constituents by diffusion from the packaging, especially where scalping or flavour degradation occurs after packaging. There is, however, the question of whether a food is being sold as fresh when this is not so. This is more a legal matter of consumer protection than a technical one as the question arises of when

Table 4.8 Substances emitted by Active Packaging

Substance	Purpose	Source	Reference
Carbon dioxide	antimicrobial	film	Rooney, 1989
Ethanol	antimicrobial	sachet	Abe, 1990
Silver ion	antimicrobial	sachet	Abe, 1990
Organic acids	antimicrobial	film	Hirata, 1992
Sulfur dioxide	antimicrobial	film	Illichkiss, 1993
Benzoyl	antimicrobial	sachet	ICI Australia
Flavours	antimicrobial	film	Halek and Garg, 1988
Hinokimol	fortification	film	Venator, 1986
BHT	antimicrobial	film	Abe, 1990
Enzymes	antioxidant	film	Han <i>et al.</i> , 1987
	various	film	Buday, 1990

flavour addition to a food fabricated from many ingredients becomes contrary to consumer interests.

Release of very few flavours has been investigated to date, although the ease of oxidation of many flavours suggests an opportunity to provide slow-release flavour precursors in the packaging material. The manufacture of flavour concentrates in the common commodity plastics has been described by Veriatour (1986). Master batches of plastics with concentrations of up to 40% of the flavour have been marketed with a view to obviate the effects of flavour scalping.

4.5.1 Antioxidant release from plastics

Two factors acting concurrently are likely to influence the use of packaging materials as sources of antioxidants in some foods. The first of these is the need of the industry to respond to pressure by some consumer advocates for reduced use of food additives (Smith, 1993). The second is the renewed interest of plastics resin manufacturers in using natural, or other approved food antioxidants in polymer stabilisation replacing some of those developed specifically for plastics. Dilaurylthiodipropionate and its base acid, thiodipropionic acid, are approved food additives in some countries and are used as stabilisers in food-grade polyethylene (Anon., 1992).

The potential for evaporative migration of antioxidants into foods from their packaging plastics has been studied by Calvert and Billingham (1979) who developed a theoretical model. This work has been taken further by Han *et al.* (1987) who determined the effect of temperature on both the diffusion coefficient of butylated hydroxytoluene (BHT) in HDPE and the rate of its evaporation into the package of oat flakes. It was found that at 39°C only 55% of the original BHT remained in the film after 1 week. The loss by outward migration was 70%, and 25% of the BHT was found in the cereal. After 6 weeks the HDPE film was free of antioxidant and 19% of that originally in the film remained in the cereal. The workers compared the impact of two starting levels in the film on oxidation of the cereal oil and found that with an initial 0.32% BHT there was less oxidation than with 0.02%.

These results of Han *et al.* (1987) demonstrate the potential for release of antioxidant into foods provided the rate of diffusion can be matched to the food's needs. The outward loss can be controlled by use of a layer of film with low permeability to the antioxidant or by use in a closure. In the case of liquid foods or solids with close-fitting packaging the process could be based on diffusion alone and not require the antioxidant to be able to evaporate.

Commercial use of this approach to antioxidant release has been reported by Labuza and Breene (1989) who noted that waxed paper has sometimes

been used as a reservoir for antioxidant release by the US cereal industry.

Other antioxidants might also be used in this way. Lignert and Eriksson (1980) found that Maillard reaction products have a strong antioxidant function. This work has been extended by Anese *et al.* (1993). The potential for applying such antioxidants to foods via packaging materials has been suggested (Eriksson, private communication).

The patent of Goyo Shiko KK (1993) describes application of amino acids and saccharides which produce reducing sugars on decomposition and perform as oxygen scavengers when used in coating or lamination of packaging films. These compositions would be expected to undergo the Maillard reactions but their rate would depend upon the thermal conditions used in preparing the packaging and any thermal processing of the packaged product. The inventors nominate liquid foods in cans as a target product area and, given the hydrophilic nature of the polymers involved, it appears likely that Maillard reaction products could be extracted into the food to act as antioxidants as well as scavengers.

It has recently been shown that polyethylene bottles stabilised with vitamin E cause less noticeable flavour in distilled water than bottles stabilised with either BHT or Irganox (a hindered amine antioxidant for polymers). There is an opportunity to investigate whether oils can be stabilised by diffusive addition of antioxidant at sustained low levels from the packaging.

The observation of Han *et al.* (1987) that BHT was lost outwards from HDPE film packs points to an otherwise unrelated opportunity for active packaging. There has been constant pressure from importers of grains and other agricultural products for reduced levels of pesticide residues in these products at the time of delivery. Packages such as sacks and lined cartons containing these products are often attacked by insects during warehousing and transport. The inclusion of low-toxicity fumigants such as pyrethrins in an outer layer of packaging material offers the opportunity to achieve sustained insecticidal activity without substantial addition of fumigant to the food. Highland and Cline (1986) found that polypropylene containing 203 mg m⁻² of permethrin provided rather similar resistance to attack by burrowing insects to that provided by polyester which has a harder, slippery surface. Their work involved exposing: polyethylene; polypropylene/polypropylene/polyethylene laminate, the latter containing permethrin in the outer layer; and polyester/polyethylene pouches of many foods, to four insect populations. The permethrin-treated pouches were resistant to two insect species for 24 months. The effect was not entirely consistent since the treated pouches failed at 24 months with one insect species and were better than polyester with one of the remaining species and worse than polyester with the other. The authors concluded that the order of descending resistance of films to the insects was permethrin-treated film, polyester film, polyethyl-

ene film and worst, polypropylene film. This work might be developed to provide a low-cost answer to some of the major problems of fumigation, including the cost of repeated fumigations with methyl bromide approximately bi-monthly, as well as reducing the exposure of staff to fumigant application conditions. The permethrin or alternative treatments would need to be submitted for regulatory approval.

It has been suggested recently that enzymes might be released into foods from packaging materials, probably to achieve effects such as antimicrobial action. Labuza and Breene (1989) have reviewed the potential for release of bound enzymes into foods. Enzyme inhibitors might also be bound to a film surface. An example would be the binding of the inhibitor of methyl esterase to the package surface to bind methyl esterase. The result might be prevention of cloud drop in fresh orange juice (R.L. Johnson, private communication). The subject of enzymes in active packaging is discussed in Chapter 7. The use of enzymes in edible coatings is discussed in Chapter 5.

4.6 Permeability modification

There are a number of circumstances in which it is desirable for the packaging material to be more permeable to one substance than to another. The importance of predicting the requirements of plastic film's permeability to carbon dioxide and oxygen in packaging of fresh horticultural produce has been discussed in Chapter 3. It is possible to modify the permeability of a window in a package and to control gas exchange through this limited area. A variety of semipermeable patches were initially developed by the Hercules company in the USA. Subsequently the effect of sorbed water on cellulose patches has been claimed to give selectivity in gas permeability matched to the respiration rates of some produce.

There are other substances which need to be selected for entry into plastics packaging. Of particular interest is the ability to selectively transmit smoke flavours through films which are useful as skins for ham and other preserved meats. These are films of polyamide alloy which are highly permeable to water and oxygen under conditions of high temperature and high humidity and highly impermeable to oxygen at room temperature under dry conditions (Nishini and Yoshii, 1988). Hirata (1992) described one such type of film as having an oxygen transmission rate of 8 ml/m²/day at 20°C, 60% RH and a water vapour transmission rate of (WVTR) 60 g/m²/day at 40°C, 90% RH. The low oxygen permeability is necessary for colour retention of preserved meats. This high WVTR should favour rapid transmission of polar flavours. Kureha Chemical Co. (1986) described a polyamide film for this purpose with an OTR in the range 50–300 ml/m²/day for film thicknesses of 5–50 µm.

4.7 Current use commercially

The commercial development of plastics-based active packaging has not occurred evenly either geographically or in terms of their field of application. The major field to date has been horticulture in which several forms of enhanced permeability films have been commercialised for both trade and home use. This success, in spite of a lack of soundly based evidence of effectiveness in many cases, owes much to substantial prior scientific research. This research into equilibrium modified atmosphere packaging has been based on the work of Kader (1980) and earlier workers including Jurin and Karel (1963). Since some of the active packaging technologies currently commercial are scarcely improvements on existing technologies there will probably be significant realignment in the marketplace. The need for active packaging solutions to problems in the storage and distribution of horticultural produce may well ensure that the development of the most soundly based technologies is commercialised. Ethylene scavenging, condensation control and equilibrium modified atmosphere packaging will continue to be emphasised.

Active packaging for processed foods is still based largely on sachet technologies, with the exception of moisture control packaging. It is in the processed food field that commercial development of plastics-based systems can be expected to be substantial over the next few years. Perhaps Toyo Seikan Kaisha's planned manufacture of an oxygen-scavenging laminate for the semi-aseptically packaged boiled-rice market by Sato Food Industry Co. Ltd is the first example. This tray has been described as 'epoch making', causing, as is planned, a 100 000 meals/day operation to be more cost effective (Anon., 1994).

The substantial impact on the marketplace of oxygen-scavenging crown seals for beverages, metallised polyester microwave susceptors and time-temperature indicator strips is discussed in other chapters.

4.8 Regulatory and environmental impacts

Since plastics-based active packaging involves not only changing current materials somewhat but also inclusion of reactive components in some cases, regulatory authorities must become involved in many developments. Indeed regulatory considerations appear to have caused the delay in the introduction of a chemical barrier to oxygen into PET beverage bottles.

The effect of environmental considerations on plastics-based active packaging will vary with the nature of the product/package combination. Commodity films used for produce packaging may become the object of recycling schemes, especially in the European Union, and so additional ingredients will need to be evaluated for their impact. Barrier packages used

for processed foods at present are generally not amenable to economic recycling. The benefits of active packaging in terms of food quality, safety and shelf-life extension will need to be considered in a holistic approach to environmental impact assessment. A study by Koopman (1994) of food packaging in the Netherlands demonstrated that 'the packaging sub-system cannot be studied or optimised in isolation'. Accordingly, active packaging plastics should be judged on the basis of their contribution to the quality and safety of food.

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5 Edible films and coatings as active layers

B. CUQ, N. GONTARD and S. GUILBERT

5.1 Introduction

Edible films and coatings are traditionally used to improve food appearance and conservation. The most common examples are wax coatings for fruit (used in China since the 12th century), chocolate coatings for confectionery, lipid films to protect meat products, and soy milk-based lipoprotein films to improve the appearance and preservation of certain foods in Asia.

Formulations for edible films or coatings must include at least one component able to form a suitably cohesive and continuous matrix. The basic materials can be classified in three categories: polysaccharides, proteins and lipidic compounds. Polysaccharides (vegetable and microbial gums, starches, celluloses and derivatives, etc.) have good film-forming properties. Films formed from these hydrophilic compounds provide efficient barriers against oils and lipids (Murray *et al.*, 1972), but their moisture barrier properties are poor. Although not as extensively studied, protein-based films have highly interesting properties. Many protein materials have been tested: collagen, zein, wheat gluten, ovalbumin, soybean casein, etc. (Guilbert and Biquet, 1989). The mechanical and barrier properties of these films are generally better than those of polysaccharide-based films; this is due to the fact that, contrary to polysaccharides which are monotonous polymers, proteins have a specific structure which confers larger potential functional properties (Guilbert and Graillie, 1994). Many lipidic compounds, such as animal and vegetable fats (natural waxes and derivatives, acetoglycerides, surface-active agents, etc.), have been used to make edible films and coatings (Guilbert and Biquet, 1989; Kester and Fenema, 1986). They are generally used for their excellent moisture barrier properties, but there can be problems concerning stability (particularly oxidation), texture and organoleptic quality (opacity, waxy taste).

Edible films and coatings formed with several compounds (composite films) have been developed to take advantage of the complementary functional properties of these different constitutive materials and to overcome their respective drawbacks. Most composite films studied to date combine a lipidic compound and a hydrocolloid-based structural matrix (Cole, 1969; Daniels, 1973; Gontard *et al.*, 1994a; Guilbert, 1986; Kamper and Fenema, 1984a, b).

Coatings are formed directly on the food product using either liquid film-forming solutions (or dispersions) or molten compounds (e.g. lipids). They

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